III. "On the Effects of Heat on Iodide of Silver." By G. F.
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College. Communicated by Professor FREDERICK GUTHRIE,
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Professor Clerk Maxwell, when discussing the expansion of matter by
heat ('Theory of Heat,' p. 8), says, "The body generally expands (the
only exception among solid bodies, as far as I am aware, is the iodide
of silver, which has been found to contract as the temperature rises)."
M. H. Fizeau, speaking of the same substance ('Nouvelles Observations
relatives à l'iodure d'argent'), writes as follows :—" Ce corps, en effet,
paraît offrir l'exemple d'une inversion complète des phénomènes ordi-
naires de la dilatation par la chaleur, car son volume diminue très-cer-
tainement pendant l'échauffement et augmente pendant le refroidisse-
ment."

It was thought that a substance possessing so marked a property
would probably exhibit peculiarities of molecular structure ; and the fol-
lowing experiments were made in order to determine whether such
peculiarities exist, to note the effects of higher temperatures upon the
iodide than those employed by Fizeau (which in no instance exceeded
100° C.), and to determine the point of maximum density of the
iodide. The phenomena which most closely approximate to those
assigned to the iodide of silver when heated are to be found in the
case of the anomalous expansion of ice and bismuth, and a few other
substances which at the moment of fusion, and for a few degrees above
their point of solidification, exhibit contraction on being heated ; but in
these instances we have to bear in mind that a change of state is simul-
taneously effected, or about to be effected, in the substance. Again,
certain crystals contract in the direction of one of their axes on the
application of heat ; but they expand in the direction of another axis,
and the total expansion is greater than the contraction, so that they
possess a positive coefficient of expansion. Garnets and a few other
crystals undergo an increase of specific gravity on being strongly heated,
and slowly recover their original density.

The iodide of silver, on the other hand, when far removed from the
point at which it undergoes any change of state, appears to exhibit con-
traction, to possess what M. Fizeau calls a "negative coefficient of
expansion ;" and this is the more remarkable when we remember
that the chlorides, bromides, and iodides of potassium, sodium, and
ammonium, and the chloride and bromide of silver expand consider-
ably when heated, more so, indeed, than the most expansible metals,
such as lead, tin, and zinc. The contraction of the iodide of silver is,
according to Fizeau, quite regular between $-10°$ C. (14° F.) and
$+70°$ C. (158° F.) ; and he calculates that the contraction is equal to
about $\frac{1}{7000}$ of its volume at 0° C. for 100° C., or, again, equal to one sixth

the expansion of platinum for 100° C. He also found that a large hexagonal crystal exhibited a very considerable contraction in the direction of the axis of symmetry, while a slight expansion was produced in a direction normal to the axis of the crystal*. The contraction was observed in the case both of the crystal, a confused crystalline mass, and an amorphous mass produced by strongly compressing the precipitated iodide until it became a hard mass capable of receiving a fine polish, and possessing a specific gravity of 5·569. Fizeau considers that the iodide possesses its maximum of volume or minimum of density at a temperature of −60° C. (−76° F.).

The iodide of silver employed in the following experiments was prepared :—(1) By precipitation. Pure iodide of potassium was added to nitrate of silver, both in dilute solution. The precipitated iodide was thoroughly washed in the dark, slowly dried, fused in a porcelain crucible, and cast into cylindrical masses, either in a warm porcelain or brass mould†. (2) By dissolving pure silver in strong hydriodic acid, evaporating to dryness, fusing. (3) By exposing pure silver leaf for several hours to the vapour of iodine produced by spontaneous evaporation.

Before we examine the effects of heat upon the iodide, it may be well to say a word or two concerning the action of light upon it. A considerable amount of misconception appears to exist in regard to this. Gmelin says " it turns brown on exposure to light, but less quickly than the chloride ; " Miller says " it is but slowly acted upon by light ; " Fizeau describes it as " noircissant lentement à la lumière ; " while Vogel (' Jahresbericht,' 1863) affirms that if it be precipitated with excess of iodide of potassium it is scarcely affected by light, whereas if precipitated with excess of nitrate of silver it changes colour, but undergoes no chemical change. The general idea that it is nearly as sensitive to light as the chloride, has no doubt arisen from the fact that iodides and chlorides are known to have many points of resemblance, and that the iodide is largely used in photography ; moreover we remember that a thin film of iodide of silver was the sensitive medium in the original daguerreotype. But we must bear in mind that the change produced by light is not apparent until the so-called " developing solution," which contains reducing agents, has been employed. The change is indeed most obscure : the author of the article on Photography in Watt's ' Dictionary of Chemistry ' says of it, " The atoms have apparently acquired a certain degree of mobility, in consequence of which, when submitted to the action of reducing agents, such as ferrous sulphate or pyrogallic acid, they suffer decomposition, the silver being reduced to the

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* " Sur la propriété que possède l'iodure d'argent de se contracter par la chaleur et de se dilater par le froid," Comptes Rendus, 1867.

† I must express my indebtedness to Mr. Valentin for allowing me to have a quantity of iodide prepared at South Kensington.

metallic state, and forming an opaque metallic film on the parts of the surface which have been exposed to light."

The following experiments were made to determine the degree of sensitiveness of the iodide to light:—

α. By means of a large lens the rays of the electric lamp were brought to a focus within a glass cell containing a solution of iodide of potassium; a solution of nitrate of silver was then introduced by a pipette at the apex of the cone of rays. The precipitated iodide possessed its usual pale yellow colour.

β. Freshly precipitated iodide in suspension, with a slight excess of iodide of potassium, remained in the full glare of a July sun without undergoing any perceptible change; neither did it subsequently darken.

γ. Freshly precipitated iodide in suspension, with a slight excess of nitrate of silver, underwent no immediate change on exposure to a July sun. At the end of an hour it had become slightly grey, and subsequently darkened.

δ. Organic matter in the shape of starch-paste did not induce any change when mixed with freshly precipitated iodide in suspension with a slight excess of iodide of potassium. Albumenized paper with iodide precipitated upon it did not undergo any immediate change.'

ε. Some dried and powdered iodide was found to have acquired a slight greyish metallic tinge after an hour's exposure to the sun. A freshly broken surface of fused iodide became very slightly darker after exposure to the sun. A very pale microscopical crystal of iodide, removed from the interior of a crystalline mass, became slightly brown after several hours' exposure to diffused light.

ζ. Crystals of iodide of silver produced by direct solution of silver in hydriodic acid were not affected by light; neither were crystals of hydro-argentic iodide (AgIHI), nor crystals of argento-potassic iodide (AgIKI).

η. A sheet of silver leaf was exposed to the vapour of iodine (produced by spontaneous evaporation) for five minutes; it possessed a faintly yellow tinge, which on exposure to the sun instantly became pale green, but on further exposure returned to its original pale yellow. A second sheet was exposed for ten minutes to the vapour of iodine; it acquired a golden-yellow surface, which on exposure to diffused light acquired a purplish-red colour, and on exposure to the sun became greenish purple. On continued exposure this colour disappeared, and the plate returned to almost the original yellow colour.

θ. A sheet of silver leaf was exposed to the vapour of iodine for half an hour, at the end of which time it possessed a decided golden yellow colour; on exposure to the sun it instantly acquired a dark purple colour, edged with green at those parts least exposed to the direct vapour of the iodine. On continued exposure the purple became paler, but the sheet did not return to its original yellow colour.

ι. A developing solution composed of ferrous sulphate, alcohol, acetic acid, and water, when applied to the exposed sheets of η and θ, which had been purple, but on continued exposure nearly regained their original colours, produced a reddish-brown colour.

κ. A sheet of silver leaf was exposed to the vapour of iodine for many hours; it was found to be converted into a slightly coherent film of lemon-yellow iodide. Light had no effect upon it, even after long exposure to a July sun; neither was any colour produced on the addition of a developing solution.

The pure iodide of silver would thus appear to be scarcely affected by light, except when silver is present, either in the form of nitrate or, as in the case of the silver films, as metallic silver.

If the precipitated iodide of silver be fused it is found to cool to a greenish-grey mass, which in thin layers is translucent. The surface has sometimes a dark steel-grey, semimetallic appearance, but this does not affect the composition. Sometimes, without any apparent cause, the ordinary greenish surface and the dark steel-grey may exist side by side in the same fused mass. A second fusion may produce a uniformly greenish surface or a uniformly steel-grey surface. But whatever the appearance of the fused mass, it always furnishes when pulverized a lemon-yellow powder, which, when heated, remains unaltered in colour up to about 105° C. (221° F.). At that temperature it begins to darken, and between 105° C. and 180° C. (356° F.) it assumes darker and darker shades of yellow, passing into orange and orange-red; above 180° C. it becomes decidedly red, and darkens through temperatures which may be roughly indicated by the fusing-points of tin, lead, and zinc, until at the latter temperature (412° C., 773° F.) it possesses a very dark brick-red colour. At this temperature the powder becomes coherent, but does not commence to fuse. At a somewhat higher temperature, probably about 450° C. (842° F.), the iodide fuses to a dark-red liquid, the colour of bromine, or of melted sulphur shortly before its boiling-point. At a red heat the iodide begins to volatilize and to decompose, and at a bright red heat this takes place readily. If the iodide be fused and poured into cold water, it becomes a lemon-yellow, amorphous, very brittle mass.

If the fused mass of iodide is allowed to cool, it solidifies to a dark-red transparent body, which is somewhat plastic. On further cooling it becomes much paler in colour, still remaining transparent; and if cooled as a thin film in contact with a hot surface, it passes to a pale yellow transparent variety. The transparent varieties, at a temperature which varies with the mass of the substance, and which in the case of a thin film may be as low as 105° C., become crystalline, opaque, and of a pale greenish-grey colour, somewhat brittle, and of a granular fracture. At the moment of the change from the amorphous, transparent, plastic variety to the opaque, brittle, crystalline variety, considerable expansion

takes place, often accompanied by a loud cracking, and large fissures appear in the mass.

Many attempts were made to determine the precise temperature at which the change from the amorphous to the crystalline condition takes place; but the results were somewhat discordant, depending apparently on the mass of the iodide, and perhaps on the number of times it had been previously fused. The iodide was fused in a glass tube or porcelain crucible, and when fusion was quite complete was placed in an air-bath at 150° C. (302° F.) and allowed to cool. The exact temperature at which the tube was broken by the expanding mass was noticed. About 15 grammes of iodide, which had been often fused, changed suddenly from the amorphous to the crystalline condition at 120° C. (248° F.). Another specimen cracked the tube at 116° C. (240°·8). A porcelain crucible containing 10 grammes of the fused iodide commenced to change at 118° C. (244°·4 F.); the crucible was violently riven open at 105° C. Two small test-tubes, about 6 millimetres diameter and each containing 2 grammes of iodide, were placed in the hot-air bath; the two masses of iodide simultaneously changed to the crystalline condition at 109° C. (228°·2 F.). On one occasion a small mass weighing 3 grammes, prepared by dissolving silver in hydriodic acid, was fused in a tube and slowly cooled. It cooled down to the ordinary temperature of the air without breaking the tube; on moving the tube, however, the mass suddenly underwent molecular change, and the tube was broken. The same iodide fused with some which had been similarly prepared suddenly changed to the crystalline variety at 121° C. (249°·8 F.). From the above results we cannot be far wrong in stating that the change from the amorphous to the crystalline variety of the iodide takes place at a temperature of about 116° C. (240°·8 F.).

Presumably heat is evolved when the amorphous modification of the iodide passes into the crystalline. Several attempts were made to ascertain this by plunging a mass of hot amorphous iodide into hot mercury, inserting a thermometer, and allowing the whole to cool, but no rise of temperature was observed at any given point of the cooling.

If the fused iodide be cast into a tube of porcelain or brass the following effects may be observed :—(a) The mass contracts considerably at the moment of solidification, the level liquid surface sinking into a deep conical depression when it becomes solid. (β) For many seconds after the solidification the solid cylinder of iodide will freely slip out of the tube, and is then seen to be red and transparent, in fact in the amorphous condition; but (γ) if the mass cools until it assumes the crystalline condition it can no longer be got out of the tube; and if the latter be of glass or porcelain, it is infallibly broken by the expansion. Hence if a mass of iodide be allowed to cool in a tube which it cannot break when it expands, it may be made to contract and slip easily out of the tube by heating it. Hence also, as the change from the amorphous

to the crystalline condition takes place at 116° C., it would appear that between the point of fusion, 450° C. (p. 100), and the temperature at which the amorphous iodide becomes crystalline it follows the ordinary law and contracts as it cools, while below that temperature (and, as will be shown, as low as $-18°$ C., $-0°·4$ F.) it expands on getting cooler, and possesses a negative coefficient. It thus appears that when the iodide is in the amorphous condition at 116° C., immediately before the change to the crystalline condition, it is at its point of maximum density.

Several unsuccessful attempts were made to burst metal bottles, after the manner of the familiar ice-experiment, by the expansion of the iodide at the moment when it passes from the amorphous to the crystalline condition. On one occasion, when a somewhat large cylindrical mass had been cast in a tube of thin brass, the latter was burst by the expanding iodide, but thick metal bottles, furnished with a screw, which was forced down into the molten mass, were not broken. Thick porcelain and glass tubes were invariably broken by the expansion ; and a good lecture experiment to illustrate the anomalous expansion is furnished by the following means. Let 20 or 30 grammes of fused iodide be cast into a thick cylindrical tube of porcelain a centimetre diameter ; in the course of a minute or two the mass has cooled down to the temperature at which it changes from the amorphous to the crystalline condition ; it then expands, cracks the tube with a loud noise, and sometimes jerks portions of the tube to a distance of several feet.

A curious effect was noticed in the case of bars of the iodide during cooling. If a bar be cast in a tube and pushed out before it begins to expand, it is seen to curve considerably during cooling. In the case of a bar 15 centimetres long by 6 millimetres diameter, the curvature was such as would be produced with a radius of 48 centimetres, and was always the same with bars of the same length and diameter. A very slight pressure resisted the tendency of the bar to curve. The effect was not due to conduction of heat from one part of the bar while the rest remained perfectly hot ; for the effect was the same whether the bar was allowed to cool on a flat copper plate, in an air-bath, or even if it were suspended by a thread of non-conducting matter. It takes place when the iodide passes from the amorphous to the crystalline condition, and is no doubt due to the inequality of strain produced between the outside portions, which first become crystalline and expand, and the internal portions, which assimilate the change less rapidly, for the iodide is a very bad conductor of heat.

It has been stated above that at the moment of solidification of a mass of iodide of silver a considerable contraction takes place. The following experiments were made in order to determine the amount of this contraction. A copper tube, which contained 105·548 grammes of mercury, was found to contain 42·080 grammes of iodide in a molten condition (say 450° C.)—that is, a little above the fusing-point

of the iodide. This would give as the specific gravity of the molten iodide 5·406. The mass was then allowed to solidify in the tube, and a large conical cavity appeared at the moment of congelation. This cavity contained 4·552 grammes of mercury, and would contain 1·8149 gramme of iodide. Hence, if the volume of the iodide before fusion be taken as 100, the volume of the resulting fused iodide will be 104·499. Or, again, 100 volumes of molten iodide contract to 95·694 volumes of the solid. The principal expansion takes place at the moment of fusion, and the expansion between 116° C. and 450° C. is not considerable. No really satisfactory method has been yet found for determining the coefficient of expansion between 116° C. and 450° C. ; but if we assume it to be equal to the mean expansion on the other side of 116° C. (of course omitting the sudden expansion which takes place when the amorphous passes into the crystalline condition), we find that a volume 1·00000 at 116° C. will become a volume of 1·01455238 at 450° C. just below the melting-point, while in passing from the solid to the liquid condition the volume increases from 1·01455 to 1·04499, an expansion = ·03044.

When a mass of iodide of silver passes from the amorphous into the crystalline condition the molecular commotion is so considerable that portions of the mass are sometimes jerked off from the ends of a bar, and large fissures appear in the mass. These are sometimes as much as half a millimetre broad and several centimetres long in a cylindrical mass weighing from 10 to 20 grammes. They penetrate to the centre of the mass, as may be shown by cooling the iodide under mercury, when the whole mass is found to be permeated by the metal. The capacity of these intercrystalline spaces was determined by allowing a known weight of iodide to pass from its amorphous to its crystalline condition beneath the surface of mercury, and again weighing.

α. 3·643 grammes AgI after thus cooling weighed 3·968 grammes.
β. 5·913   „   „   „   „   6·417   „

And as we know the specific gravity of mercury and of the iodide, it is easy to deduce from the above that the volume of the cracks is represented respectively by (α) ·1353 gramme and (β) ·2098 gramme of iodide ; hence

$$\alpha.\ 3\text{·}643\ :\ \text{·}1353\ :\ :\ 100\ :\ 3\text{·}7112$$
$$\beta.\ 5\text{·}913\ :\ \text{·}2098\ :\ :\ 100\ :\ 3\text{·}5481$$

which give a mean of 3·6296. Therefore 100 grammes of iodide in the amorphous condition produce, in passing into the crystalline condition, intercrystalline spaces capable of containing 3·6296 grammes of iodide. From an observation which was made on a cylindrical mass of iodide a centimetre diameter, which in undergoing expansion in the passage from the amorphous to the crystalline condition had produced a separation amounting to half a millimetre in a tube which had yielded to the expansion, the expansion of the mass, *plus* the intercrystalline spaces within

it, was found to be ·047619 ; hence a volume of amorphous iodide represented by unity becomes a volume of 1·047619 in passing into the crystalline condition, *plus* the intercrystalline spaces ; and the volume of these spaces having been determined above, we find that the actual change of volume which takes place simultaneously with the change of molecular condition amounts to ·011323 ; that is, a volume of iodide at its point of maximum density (116° C.) represented by unity becomes a volume of 1·011323 in changing to the crystalline condition.

Frequent fusion and cooling appear to render a mass of iodide more brittle and crystalline, and to promote the formation of large fissures. The iodide prepared by dissolving silver in hydriodic acid and subsequent fusion was less brittle than that produced by precipitation and frequently fused. We have before noticed that while the latter passes into its crystalline condition at a temperature ranging a few degrees on either side of 116° C., the former may sometimes be cooled to much lower temperatures without change ; in fact it appears to be altogether more compact and horny and freer from intercrystalline spaces than the fused iodide produced by precipitation, indeed almost perfectly free. The specific gravity appears also to be slightly higher. Boullay found the specific gravity of the fused iodide produced by precipitation to be 5·61 ; but he was probably unaware of the presence of the intercrystalline spaces, or he did not take special precautions to obviate them. An ordinary fused mass of iodide was found to have a specific gravity of 5·545, when no precautions were taken to dislodge the air from the intercrystalline spaces. Now we have already given reasons for believing that a volume of iodide at its maximum density (116° C.) becomes a volume of 1·047619 in changing to the crystalline condition ; and if we take the specific gravity to be 5·816 at the maximum density, we deduce the specific gravity in the crystalline condition, not taking into account the intercrystalline spaces, to be 5·561,

$$1·0476 \quad : \quad 1 \quad : : \quad 5·816 \quad : \quad 5·561,$$

a number which differs by only 0·016 from the specific gravity found by direct weighing, when no precautions were taken to dislodge air from the intercrystalline spaces. When, however, the mass of iodide was boiled for a length of time in water and cooled in a good vacuum, the specific gravity at 0° C. was found to be 5·681. Deville found it under the same conditions to be 5·687[*]. The specific gravity of the molten iodide has been shown above to be about 5·406, and the specific gravity at the point of maximum density of the amorphous iodide would appear to be 5·8167. This applies to the precipitated iodide which had been several times fused, and with which the principal experiments herein described were made. A specimen of iodide produced by the direct solution of silver in hydriodic acid gave a specific gravity of 5·812, and appeared to be less crystalline

[*] " Sur les propriétés de l'iodure d'argent," Comptes Rendus, vol. lxiv.

and more compact than that produced by precipitation.   Deville found the
specific gravity of the unfused precipitated iodide to be 5·807, and of the
fused iodide 5·687, while Damour found the native crystals to have· a
specific gravity of 5·667 ; hence the amorphous precipitate has a higher
density than either the fused crystalline iodide and their native crystals.
Thus the density of the amorphous precipitate coincides almost perfectly
with the density of the fused iodide at its point of maximum density
(116° C.) when in the amorphous condition, as deduced from the above
experiments.

If we place in a specific-gravity flask a quantity of fused iodide of
silver, fill it up with mercury (taking every precaution to displace the air
from the intercrystalline spaces), and place in the ground neck of the
flask a perforated stopper continued as a capillary thermometer-stem, we
have obviously a thermometer in which we can observe the effect pro-
duced by the anomalous contraction of the iodide on the regularly
expanding mercury.   On applying heat to such an arrangement we
observe that for a while the mercury rises in the stem, until on further
heating the contraction of the iodide exceeds the expansion of the mercury,
and the column retreats if much iodide is present into the very bulb of
the instrument.

If the heating be now discontinued the mercury slowly rises as the
iodide cools, until the contraction of the mercury exceeds the expansion
of the iodide, beyond which point the mercury continues to sink as the
bulb cools.   Nothing could better illustrate the complete inversion of the
effects usually produced by heat on bodies in the case of the iodide of
silver.

Professor Guthrie suggested to me that a convenient method of deter-
mining the amount of contraction produced by heat in the iodide would
be to fill a specific-gravity flask with mercury, and determine the amounts
of mercury exuded from the flask for every ten or twenty degrees of
temperature ; then to place in the flask a known weight of fused iodide
with a known weight of mercury, and repeat the determinations.   This
was accordingly done.   About 440 grammes of mercury were employed,
and weighings made at intervals of a few degrees.   The method was
found to be satisfactory, and the results concordant.   For example (to
take a few instances from many), the amounts of mercury driven from
the flask by expansion for 10° C. were found to be as follows :—

Between 29° C. and 53° C.....·066062
   ,,   22° C.   ,,   74° C.....·067250
   ,,   20° C.   ,,   84° C.....·067390
   ,,   29° C.   ,,   86° C.....·068526
   ,,   47° C.   ,,   84° C.....·069297

numbers which, when the necessary corrections have been made for

the expansion of the glass, agree very well with Regnault's determinations of the absolute expansion of mercury. Then 38·3680 grammes of the fused iodide were placed in the flask; it was filled up with mercury, the whole was heated, cooled in a good vacuum, weighed, cooled to −18° C. (−0°·4 F.) and weighed. The flask was then heated respectively to 0° C., 21° C., 67° C., and the weights determined. At high temperatures the mercury acts upon the iodide and a green iodide of mercury is formed. The results were not very concordant above 67° C. and have not been introduced. The general results were as follows: the amounts of mercury driven from the flask for 1° C. were respectively—

Between −18° and   0° C. = ·052648
,,   −18° ,, +21° C. = ·051392
,,   0° ,, +21° C. = ·050285
,,   −18° ,, +67° C. = ·049684
,,   0° ,, 67° C. = ·048873
,,   +21° ,, 67° C. = ·048228

Now from the known weight of mercury in the flask and the known expansion of mercury, it is easy to deduce the quantity of mercury which ought to have been driven from the flask by expansion for any number of degrees; and having determined the actual amount of mercury expelled, we at once find the contraction of the known weight of iodide of silver from known number of degrees by subtracting the amount of mercury expelled from the amount of mercury which ought to have been expelled if the iodide had not been present. We can thus arrive at the coefficient of contraction of the iodide for one degree Centigrade. This appears to be ·00000718 for temperatures between −18° C. and 0° C., ·00003297 for temperatures between 0° C. and 21° C., and ·00005570 for temperatures between 21° and 67° C. Thus the coefficient augments with the temperature. The following Table (p. 107) represents the relationship between the effects of heat on iodide of silver and on mercury. It cannot be regarded as more than an approximation until more perfect methods for investigating the actions can be devised. The extreme peculiarities of the molecular constitution of the iodide, combined with the fact that it cannot be raised to a high temperature in mercury without suffering decomposition, and that its fusing-point is above the boiling-point of mercury, render experiments of this nature, especially when a high temperature is required, unsatisfactory.

TABLE showing approximately the Action of Heat on Iodide of Silver, between −18° C. and the fusing-point, compared with the Action of Heat on Mercury.
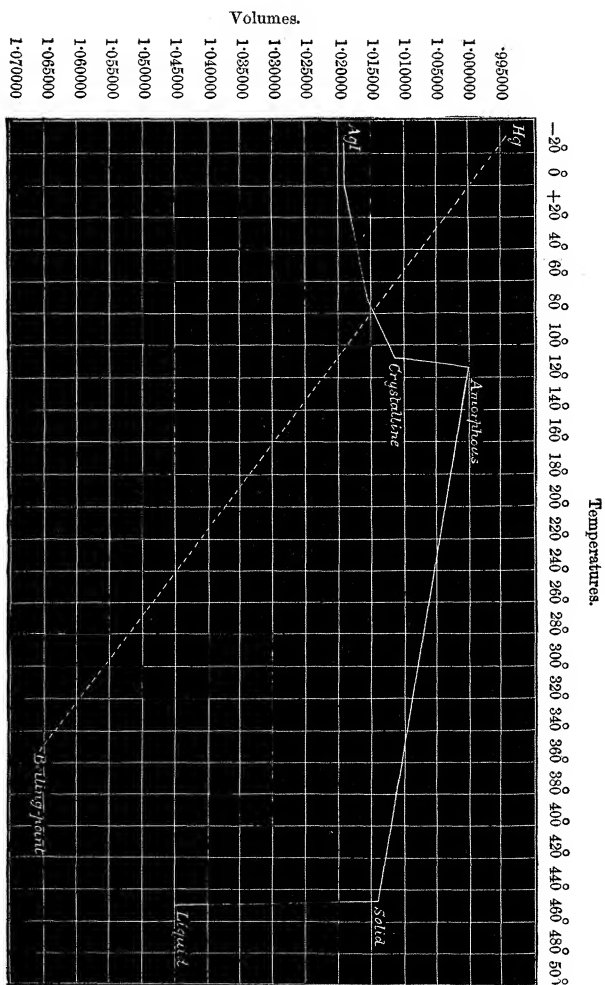
I have endeavoured to prove in the foregoing pages the following main facts :—

1. That the iodide of silver exists in three allotropic forms, viz. (α), at temperatures between 116° C. and its fusing-point, as a plastic, tenacious, amorphous substance possessing a reddish colour and transparent to light ; (β), at temperatures below 116° C., as a brittle, opaque, greenish-grey, crystalline mass ; and (γ), if fused and poured into cold water, as an amorphous, very brittle, yellow, opaque substance.

2. That the iodide possesses a point of maximum density at or about 116° C. at the moment before passing from the amorphous into the crystalline condition.

3. That if we allow a mass of molten iodide to cool, the following effects may be observed :—(a) at the moment of solidification a very considerable contraction takes place ; (β) the solid, on further cooling, undergoes slight and regular contraction after the manner of solid bodies in general, until (γ) at or about 116° C. it undergoes sudden and violent expansion, passing from the amorphous into the crystalline condition ; (δ) after undergoing this expansion the mass on further cooling undergoes slight expansion, and (ϵ) the coefficient of contraction diminishes as the temperature decreases (or otherwise expressed, the coefficient of contraction augments with the temperature).

I must, in conclusion, express my great indebtedness to Dr. Guthrie for allowing me to carry out many of the foregoing experiments in the Physical Laboratory at South Kensington.

IV. "On the Coefficient of Expansion of a Paraffine of high boiling-point." By G. F. RODWELL, F.R.A.S., F.C.S., Science Master in Marlborough College. Communicated by Prof. STOKES, Sec. R.S. Received November 17, 1874.

In the search for a liquid of high boiling-point which could be used for the exact determination of the coefficient of expansion of iodide of silver, and which at the same time should be free from certain objections which apply to the employment of mercury for this purpose, a paraffine of high boiling-point naturally suggested itself. Mr. W. H. Hatcher, to whom I express my acknowledgments, procured for me a specimen of paraffine which was taken from one of the stills at Messrs. Price's works at a high temperature. With it the following experiments were made.

The paraffine in question is perfectly white and pearly, and in thin layers translucent ; it fuses to a colourless liquid, which slightly darkens when heated for some time to a temperature exceeding 600° F. (315°·55 C.). Its specific gravity at 32° F. (0° C.) is ·921. It is hard and somewhat granular when broken, and at a low temperature may be crudely pulverized by a blow. At temperatures exceeding 100° F.

TABLE showing approximately the Action of Heat on Iodide of Silver, between −18° C. and the fusing-point, compared with the Action of Heat on Mercury.